

Complexation of Transition Metals by 3-Azidopropionitrile. An Electrospray Ionization Mass Spectrometry Study

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Most complexes of azides and transition metals involve the N_3^- azide anion as a ligand other than an organic azide. Complexes of organic azides with metals are involved in biological applications and in the deposition of nitrenes on metal surfaces, producing nitride layers for semi-conductors preparation; this makes the study of these interactions an important issue. This work describes a study of the complexation of nickel and cobalt by 3-azidopropionitrile by means of electrospray ionization mass spectrometry (ESI-MS). Complexes were obtained from solutions of NiCl_2 and CoCl_2 in methanol/water. In the case of nickel, other NiX_2 salts were investigated (where $\text{X} = \text{Br}$ or NO_3) and other solvents were also studied (notably ethanol/water). All complexes detected were single positively charged, with various stoichiometries, some resulted from the fragmentation of the ligand, the loss of N_2 , and HCN being quite common. The most abundant cations observed were $[\text{Ni(II)AzAzX}]^+$, where $\text{X} = \text{Cl}$, Br , NO_3 . Some of the complexes showed solvation with methanol/ethanol/water. Metal reduction was observed in complexes where a radical was lost, resulting from the homolytic cleavage of a metal–nitrogen bond. Collision induced dissociation (CID) experiments followed by tandem mass spectrometry (MS-MS) analysis were not absolutely conclusive about the coordination site. However, terminal ions observed from the fragmentation routes were explained by a proposed gas-phase mechanism. Density functional theory calculations were carried out and provided structures for some complexes, pointing to the possibility of 3-azidopropionitrile acting as a mono- or a bidentate ligand. (J Am Soc Mass Spectrom 2007, 18, 453–465) © 2007 American Society for Mass Spectrometry

Azides are highly reactive, unstable compounds whose chemistry has attracted the interest of chemists since 1864 when phenyl azide was discovered [1]. A great number of azides are explosive. Sodium azide is considered an excellent propellant whilst heavy metal azides, such as $\text{Pb}(\text{N}_3)_2$, are considered primary explosives [2]. Inorganic azides, in partic-

ular sodium azide, have been used in an extensive list of applications: notably as automobile air bags and airline safety chute inflators, as biocides, as radical scavengers [3], as intermediates in semiconductor preparation [4], and as enzyme inhibitors by metal center complexation of metalloproteins [5, 6]. Metal complexation is usually accomplished by N_3^- moiety. In the preparation of semiconductors, a metal azide is the precursor of the related nitride layers and epitaxial films on substrates.

Nowadays, organic azides play an important role as an interface between chemistry, biology, medicine, and materials science [7]. Industrial relevance of organic azides began with their application as intermediates in organic synthesis [8, 9]. They also become important

Published online November 30, 2006

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precursors for nitrenes, used in both nitride film deposition [10, 11] and sidewall functionalization of single-wall carbon nanotubes (SWNTs) [12, 13]. Pharmaceutical applications include the anti-HIV medication AZT (3'-azido-2',3'-dideoxy-thymidine) [14] and tuberculosis medication [15]. Some organic azides have several features that make them suitable for tagging biological molecules [16, 17].

Among the organic azides, the aromatic azides have received more attention than the aliphatic azides, which represent the second most important class of organic azides [7]. This prompted a number of us to investigate some aliphatic azides. An important feature in the reactivity of organoazides is the loss of molecular nitrogen, which can be induced thermally, photochemically, or catalytically by acid or transition metals [18–20]. In spite of their instability, some spectroscopic studies have been performed to monitor their decomposition [21–25]. Some of the aliphatic azides spectroscopically investigated, such as, azidoacetic acid, azidoacetone, and azidonitriles, have been selected for studies of their decomposition on surfaces. So far, azidoacetic acid is the only aliphatic azide for which a surface study of its decomposition has been completed [26]; previously, hydrazoic acid had been investigated as a precursor in semiconductor preparation [27–29]. Azidoacetonitrile and other aliphatic azides have also been investigated but the results are still unpublished [30]. Related to this work, Balteanu et al. [31] investigated gas-phase reactions of rhodium clusters with azidoacetonitrile as a function of cluster size and charge state to explore the reactions and surface-activated decomposition of one aliphatic covalent azide. These studies show that some applications of organic azides involve the interaction with metals, not only in semiconductor preparation but also in the synthesis of imido species in organometallic chemistry. When inorganic azides function as enzyme inhibitors, the replacement of the inorganic azide, which are toxic, by an organic azide, could be beneficial. The latter are better tolerated under physiological conditions and are relatively inert in the biological medium [17].

In the present work, complementary insight on the reactivity of azides towards metals was sought through complexation studies. Although the formation of complexes involving organic azides and transition metals has been previously investigated [32–34], the coordination site and coordination number are still matters of debate and deserve further attention. The work reported in references [32, 33] showed that the ligands, phenyl, and substituted phenyl azides, coordinate metal centers only by the terminal nitrogen of the azido group. In both cases, upon molecular nitrogen extrusion, the metal is coordinated by the alkylated nitrogen. However, when another functional group is present besides the azido group [34], the complex seems to be bidentate. In this case it is observed that the azido group coordinates by the alkylated nitrogen of the azido group.

This state of affairs prompted us to investigate the coordination chemistry of the above mentioned organic aliphatic azides, to try to make a contribution to clarify the behavior of bifunctional organoazides as ligands. In this work, 3-azidopropionitrile was used as the ligand and two transition metals were chosen, nickel and cobalt. Nickel complexation has been extensively studied in solution and in the gas phase because of its importance in biological processes [35].

The study was extended to cobalt, which always occurs in nature in association with nickel [36]. Due to their electronic configurations (unfilled 3D shells), and to the fact that they are neighbors in the first transition-metal row, they are expected to have similar chemical behavior. Currently, a similar study of azidoacetone is in progress. Also, by studying complexes with ligands with functional groups with different heteroatoms, a better understanding of these metal complexes will be obtained.

Electrospray ionization (ESI) is a soft ionization technique, which has been shown to have the ability to transfer solvated ions from solution to the gas phase. Therefore, ESI mass spectrometry is particularly suitable to study metal ions complexed by organic ligands in the gas phase [37, 38] and consequently was chosen to carry out this study.

The aim of this work is the investigation of the transition metals complexation by 3-azidopropionitrile by means of ESI-MS. In addition, attempts were made to identify the coordination site of the azide by tandem mass spectrometry. However, a contribution from density functional theory (DFT) calculations was necessary to clarify these structural features in some complexes. Ultimately, we hoped to investigate whether there is any correlation between the coordination site and the interaction site of the azide to metal clusters.

Experimental

Mass Spectrometry

3-Azidopropionitrile was synthesized and characterized using published methods [22, 39]. To avoid its decomposition, it was stored at dry ice temperature and, when used in experiments, the sample was maintained at room temperature and shielded from light to prevent photolysis.

The metallic salts used in this study were: nickel chloride hexahydrate (97%, Riedel-del-Haën, Hamburg, Germany), nickel bromide (98%, Merck, Madrid, Spain), nickel nitrate hexahydrate (97%, Aldrich, Madrid, Spain) and cobalt chloride (97%, Aldrich), which were used without further purification. Methanol and ethanol (99.9%, Merck) HPLC grade, and doubly distilled water were used as solvents.

Solutions 5 mmolL⁻¹ of NiCl₂, NiBr₂, Ni(NO₃)₂, and CoCl₂ were prepared in a 1:1 water/methanol (vol/vol) solvent mixture as well as in a water/ethanol solvent mixture (vol/vol). To the salt solu-

tions, 3-azidopropionitrile was added until the whole solution became 65 mmol L^{-1} in 3-azidopropionitrile.

All experiments were performed using a LCQ Duo ion trap mass spectrometer from Thermo Finnigan (San Jose, CA) equipped with an electrospray ion source. Samples were introduced, via a syringe pump (flow rate of $5 \mu\text{L/min}$), into the stainless steel capillary of the electrospray ion source. The applied spray voltage in the source was 4.5 kV, the capillary voltage was 10 V, and the capillary temperature was 220°C . All the other mass spectrometer parameters, as well as those above, were adjusted to optimize the signal-to-noise ratios for the ions of interest. Nitrogen was used as nebulizing and drying gas in the source.

The pressure measured during experiments at the skimmer cone with a convectron gauge was normally $1.59 \times 10^2 \text{ Pa}$. The base pressure in the ion trap with helium added was typically $1.49 \times 10^{-3} \text{ Pa}$.

All mass spectrometry data were acquired in the positive ion mode, the full scan spectra were recorded in the range m/z 50 to 500, and three microscans were averaged. The only exception was for bromide spectra, for which the mass range was 50 to 600, to encompass all species of interest detected for chloride. Collision induced dissociation (CID) and MS-MS experiments were performed with helium, at various resonant excitation amplitude values requiring excitation voltages in the range 0.75 to $1.1 V_{p-p}$. The collision energy was gradually increased until the precursor and the product ions could both be observed in the MS-MS spectrum, but the precursor peak intensity was reduced 50 to 20% of its original height. Injection times were 50 ms in a full scan and 200 ms in a MS-MS scan. Xcalibur software (San Jose, CA) was used to acquire and process the data.

Theoretical Calculations

Density functional theory (DFT) [40] calculations for mono- positively charged complexes involving 3-azidopropionitrile and Ni are reported. Geometry optimizations were carried out with the hybrid B3LYP functional, which is a combination of the Becke's three-parameter exchange functional (B3) [41] with the Lee, Yang, and Parr (LYP) [42] correlation functional. All the calculations were carried out with the 6-31 ++ G(d,p) basis set [43, 44]. Single-point energy calculations using the B3LYP/6-31 ++ G(d,p) optimized structures were carried out with the 6-311 ++ G(d,p) basis set [45, 46]. Full geometry optimizations and frequency calculations were carried out for all the complexes. The main purpose of these theoretical calculations is to provide information on the coordination chemistry of the complexes. All calculations were carried out with the Gaussian-03 [47] suite of programs.

Results and Discussion

Mass Spectrometry Study

The first step in this experimental work was to optimize the ESI mass spectrum obtained from a solution of 3-azidopropionitrile in methanol/water. Upon addition of a nickel salt, a great change in the number of peaks was observed; most of them were real envelopes of peaks at m/z values above the molecular mass of 3-azidopropionitrile (96 Da), showing that the azide had reacted with the metal. In fact, the envelopes of peaks revealed different isotopic patterns, probably due in part to the presence of nickel isotopes.

The next step is the identification and assignment of the observed species. The complex ions, obtained from a solution of 3-azidopropionitrile and nickel chloride in methanol/water as solvent, were assigned and are presented in Table 1. This Table contains only the monoisotopic masses of each complex ion observed for different systems studied. The first approach for assignments was to combine the overall charge, the monoisotopic mass of the ion, and the isotopic pattern of the envelope. A remarkable feature is that all complex species observed are single positively charged. However, some doubly charged species were observed but with a very low abundance ($\leq 1\%$) and because of this they were disregarded. As the main complexes always include chlorine and nickel, natural isotopic abundances were considered to compare expected and experimental isotopic patterns.

Three routes were adopted to confirm the assignments made for 3-azidopropionitrile and nickel chloride in methanol/water. They were change of solvent, change of counter ion, and CID experiments. As some of the complexes are solvated with methanol or water, some experiments were performed only with water as a solvent, as three molecules of methanol equal 96 Da, which is the molecular mass of 3-azidopropionitrile. This experiment was useful to solve the above ambiguity and to confirm solvation with methanol, since m/z 349, 317, 221, 158 (Table 1) disappear from the spectrum. The presence of methanol was checked twice through an additional experiment using a different solvent mixture: ethanol/water. A second way to seek confirmation of the composition of the complexes was to carry out experiments with nickel bromide and nickel nitrate, in this case proving the presence of chlorine as a ligand. Finally, another transition metal, cobalt, was used.

CID experiments followed by MS-MS analysis were performed to fulfil two requirements. First, as a tool to investigate the coordination site and second, as an indirect confirmation of the assignments. All these topics will be addressed in the next section of the paper.

Isotopic Analysis for Ion Assignment

The first approach, applied for identification of the complex ions observed, was based on isotopic patterns. Thus, the assignments were accomplished by

Table 1. Parallel assignment of nickel complexes with 3-azidopropionitrile from NiCl₂, NiBr₂ and Ni(NO₃)₂ solutions

Complex ion composition	X = Cl		X = Br		X = NO ₃	
	<i>m/z</i>	Rel. abund. (%)	<i>m/z</i>	Rel. abund. (%)	<i>m/z</i>	Rel. abund. (%)
[Ni ₂ (II)AzAzX ₃] ⁺	413	12	545	8	494	3
[Ni ₂ (II)Az(Az-N ₂)X ₃] ⁺	385	3	517	1	—	—
[Ni(II)AzAzAzX] ⁺	381	11	425	14	408	3
[Ni(II)AzAz(Az-N ₂)X] ⁺	353	9	397	1	—	—
[Ni ₂ (II)AzX ₃ CH ₃ OH] ⁺	349	4	481	3	—	—
[Ni ₂ (II)AzX ₃ H ₂ O] ⁺	335	4	467	21	—	—
[Ni(II)AzAzXCH ₃ OH] ⁺	317	16	361	11	344	3
[Ni(II)AzAzXH ₂ O] ⁺	303	46	347	32	—	—
[Ni(II)AzAzX] ⁺	285	100	329	56	312	100
[Ni(II)Az(Az-N ₂)X] ⁺	257	9	301	3	—	—
[Ni(II)(Az-N ₂) ₂ X] ⁺	229 ^a	17	273	4	256	2
[Ni(II)AzXCH ₃ OH] ⁺	221	7	265	15	248	9
[Ni(II)AzXH ₂ O] ⁺	207	20	251	22	234	16
[Ni(II)AzX] ⁺	189 ^a	14	233	25	216	8
[Ni(II)(Az-N ₂)(Az-CH ₂ N ₃)] ⁺	166	20	166	1	166	1
[Ni(II)(Az-N ₂)X] ⁺	161	16	205	6	188	3
[Ni(II)(Az-N ₂)CH ₃ OH] ⁺	158	14	158	4	158	1
[Ni(II)(Az-N ₂)H ₂ O] ⁺	144	32	144	17	144	7
[Ni(II)(Az-CHN ₃)X] ⁺	134	5	178	5	161	1
[Ni(II)(Az-N ₂)] ⁺	126 ^b	71	126	40	126	9
[Ni(II)(Az-CH ₂ N ₃)H ₂ O] ⁺	116	3	116	2	116	3
[Ni(II)(Az-CHN ₃)] ⁺	99	11	99	13	99	2
[Ni(II)(Az-CH ₂ N ₃)] ⁺	98	12	98	7	98	1

^aThe corresponding [M+2] ions have more than one contribution.^bThe corresponding [M+1] ion has more than one contribution.

combining the mass and charge and also the possible arrangements of constituent elements with several isotopes. In this work, M is attributed to the monoisotopic mass of an envelope related with one complex. All the assignments are compiled in Table 1 in which 3-azidopropionitrile is designated as Az for simplicity. These assignments, based on isotopic patterns, were also confirmed by MS-MS experiments. These experiments were developed mainly for the purpose of identifying the coordination site, and they will be described later in the paper. Nevertheless, the results from them were useful to elucidate the identification of the complexes.

Ions at *m/z* 189 and 229 show higher abundances than expected on the grounds of the isotopic patterns, for corresponding M + 2 ions (*m/z* 191 and 231). The same applies to the M + 1 ion corresponding to [Ni(I)(Az-N₂)]⁺ (*m/z* 126). This points to the possibility of more than one contribution to the mentioned ions.

However, MS-MS experiments were not conclusive on the composition of the additional contribution. The *m/z* 127 signal may receive two contributions, one as M + 1 of ion at *m/z* 126, and another from a possible complex with the following composition [Ni(I)(Az-HCN)]⁺.

Substitution of the Solvent

Other support for the proposed assignments was sought for complex ions solvated with methanol, replacing methanol in the solvent mixture with ethanol. If the assignments were correct, a displacement of 14 Da was expected for the corresponding peaks of solvated ions, while the peaks of the non-solvated complex should remain at the same values of *m/z*. Actually, all nonmethanol-solvated complexes remained unchanged, thus confirming the assignments. Complexes at *m/z* 349, 317, 221, 158 were displaced to *m/z* 363, 331, 235, 172 as expected according to the

Table 2. Parallel assignments of resulting complex ions in methanol/water and ethanol/water solvent mixtures (NiCl₂ solutions)

Methanol:water		Ethanol:water	
Composition assignment	<i>m/z</i>	Composition assignment	<i>m/z</i>
[Ni ₂ (II)AzCl ₃ CH ₃ OH] ⁺	349	[Ni ₂ (II)AzCl ₃ CH ₃ CH ₂ OH] ⁺	363
[Ni(II)AzAzClCH ₃ OH] ⁺	317	[Ni(II)AzAzClCH ₃ CH ₂ OH] ⁺	331
[Ni(II)AzClCH ₃ OH] ⁺	221	[Ni(II)AzClCH ₃ CH ₂ OH] ⁺	235
[Ni(II)(Az-N ₂)CH ₃ OH] ⁺	158	[Ni(II)(Az-N ₂)CH ₃ CH ₂ OH] ⁺	172

existing assignment (Table 2). This means that methanol or ethanol are present in the coordination sphere(s) of these complexes.

Substitution of the Nickel Salt

The vast majority of complexes, listed in Table 1, have chloride ion as a ligand. This prompted us to change the nickel salt to establish the existence of chloride as a ligand. Two different salts were used: nickel bromide and nickel nitrate. In the case of nickel bromide, if it had a similar behavior to the chloride, all complexes with chloride ligands should be shifted by 44 Da per bromide present in the complex. The results obtained under these new conditions present the expected behavior with respect to the assignments and results given in Table 1 for the chloride. Given, the unaltered m/z values for species without chloride as a ligand, and the corresponding shift in the others, further support was obtained for the assignments reported in Table 1. In other words, either of the counter ions is one of the ligands in these species. Obviously, the relative intensity of the related peaks change when NiBr_2 is used, especially due to the ionic radii and different natural isotopic abundance of Br^- relative to Cl^- , but all species previously identified are present in the spectra. Again, for the ions observed with bromide, isotopic analysis and MS-MS experiments were performed for the sake of confirmation. The behavior was in agreement with that observed for chloride.

Another different counter ion, nitrate, was chosen. Its composition and structure is different from the halides already tested. It is composed of atoms of a different nature, it has a greater volume, and thus it may contribute different information to a better understanding of the complexation. In the literature $\text{Ni}(\text{NO}_3)_2$ has been reported as one of the salts used in nickel complexation [48]. In addition, it is known that it can act as a monodentate or bidentate ligand [49], unlike the halide anions that function only as monodentate ligands. In this work, some nitrate complexes were observed (Table 1) which, when compared with chloride and bromide complexes, the basic differences were the relative abundances, which were mostly very low in the nitrate case. All detected complexes have abundances up to 17%, except the complex at m/z 312 with 100% abundance attributed to $[\text{Ni}(\text{II})\text{AzAzNO}_3]^+$. For equivalent complexes, a 27 Da difference meant a replacement of one chloride by one nitrate. When no shift was detected, this was indicative of the absence of a counter ion as a ligand. Due to the particular properties of nitrate as a ligand, when compared with Cl^-/Br^- , some new ionic species were observed to be formed, i.e., $[(\text{Az-N}_2)\text{Ni}(\text{I})\text{O}]^+$ and $[(\text{Az-CHN}_3)\text{Ni}(\text{I})\text{O}]^+$ at m/z 142 and 115, respectively. In this nitrate study, the assignments were also confirmed by isotopic patterns and

MS-MS experiments, the isotopic pattern being mainly dependent on the nickel isotopic pattern.

Substitution of the Metal

A study with cobalt instead of nickel was performed under the same experimental conditions as described above. The study had inherent importance since the complexation of cobalt by 3-azidopropionitrile was investigated for the first time. Also, it added important insight to the general aim of this work. Furthermore, cobalt has no isotopes, unlike nickel, so it may provide complementary spectral information. This is more important from the point of view of a contribution to the understanding of the structure of the metal complexes than the confirmation of assignment of the ion signals as those had already received confirmation through different routes.

Comparing the data obtained with CoCl_2 and the previous data with NiCl_2 (Table 3), the same type of complexes were detected for Co but shifted 1 or 2 Da, as in the complex there are one or two Co atoms. This result proves unequivocally the capacity of 3-azidopropionitrile to form complexes with transition metals. In the case of complexes with Co, the isotopic patterns observed are basically dependent on the isotopic pattern of the counter ion Cl^- . The complex $[\text{Co}(\text{I})(\text{Az-N}_2)]^+(m/z$ 127) shows a similar behavior to the complex at m/z 126 for Ni, concerning the intensity of the peak at $M+1$. In this case, an ion signal at m/z 128 may receive two contributions, one from $M+1$ ion at m/z 127 and another from a possible complex with the following composition $[\text{Co}(\text{I})(\text{Az-HCN})]^+$.

In summary, from the comparison of the data obtained for Ni and Co, besides the conclusions already mentioned above, the occurrence of Ni(II) or Ni(I) and Co(II) or Co(I) in the complex species was proven. In general, for both studies, a greater variability of the relative intensities, in the full mass spectra, for peaks associated with ions of low m/z ($m/z < 200$ Da) and low abundances was observed. Some of the ions at $m/z < 200$ Da result from the decomposition of complex ions at higher m/z .

MS-MS Analysis

This analysis was intended to achieve two requirements. The first one, described above, was to confirm the assignment of the ionic signals through the losses resulting from CID experiments. The second one viewed the CID of a given complex ion, followed by MS-MS analysis, as a tool to search for the coordination site(s). The latter objective is going to be the focus in this section.

The fragmentation sequences, shown in Scheme 1 and Scheme 2, were obtained by mass selection of all the corresponding precursor ions and their fragmentation. The occurrence of ion-molecule reactions in the

Table 3. Parallel assignments of resulting complex ions in NiCl₂ and CoCl₂ solutions (solvent mixture methanol/water)

Complex ion composition	M = Ni		M = Co	
	<i>m/z</i>	Rel. abund. (%)	<i>m/z</i>	Rel. abund. (%)
[M ₂ (II)AzAzCl ₃] ⁺	413	12	415	41
[M ₂ (II)Az(Az-N ₂)Cl ₃] ⁺	385	3	387	2
[M(II)AzAzAzCl] ⁺	381	11	382	3
[M(II)AzAz(Az-N ₂)Cl] ⁺	353	9	—	—
[M ₂ (II)AzCl ₃ CH ₃ OH] ⁺	349	4	351	33
[M ₂ (II)AzCl ₃ H ₂ O] ⁺	335	4	337	20
[M(II)AzAzClCH ₃ OH] ⁺	317	16	318	75
[M(II)AzAzClH ₂ O] ⁺	303	46	304	100
[M(II)AzAzCl] ⁺	285	100	286	66
[M(II)Az(Az-N ₂)Cl] ⁺	257	9	258	3
[M(II)(Az-N ₂) ₂ Cl] ⁺	229 ^a	17	230	1
[M(II)AzClCH ₃ OH] ⁺	221	7	222	89
[M(II)AzClH ₂ O] ⁺	207	20	208	26
[M(II)AzCl] ⁺	189 ^a	14	190	50
[M(II)(Az-N ₂)(Az-CH ₂ N ₃)] ⁺	166	20	167	11
[M(II)(Az-N ₂)Cl] ⁺	161	16	162	45
[M(I)(Az-N ₂)CH ₃ OH] ⁺	158	14	159	33
[M(I)(Az-N ₂)H ₂ O] ⁺	144	32	145	33
[M(II)(Az-CHN ₃)Cl] ⁺	134	5	135	20
[M(I)(Az-N ₂)] ⁺	126	71	127	54
[M(II)(Az-CH ₂ N ₃)H ₂ O] ⁺	116 ^b	3	117	28
[M(I)(Az-CHN ₃)] ⁺	99	11	100	14
[M(II)(Az-CH ₂ N ₃)] ⁺	98	12	99	9

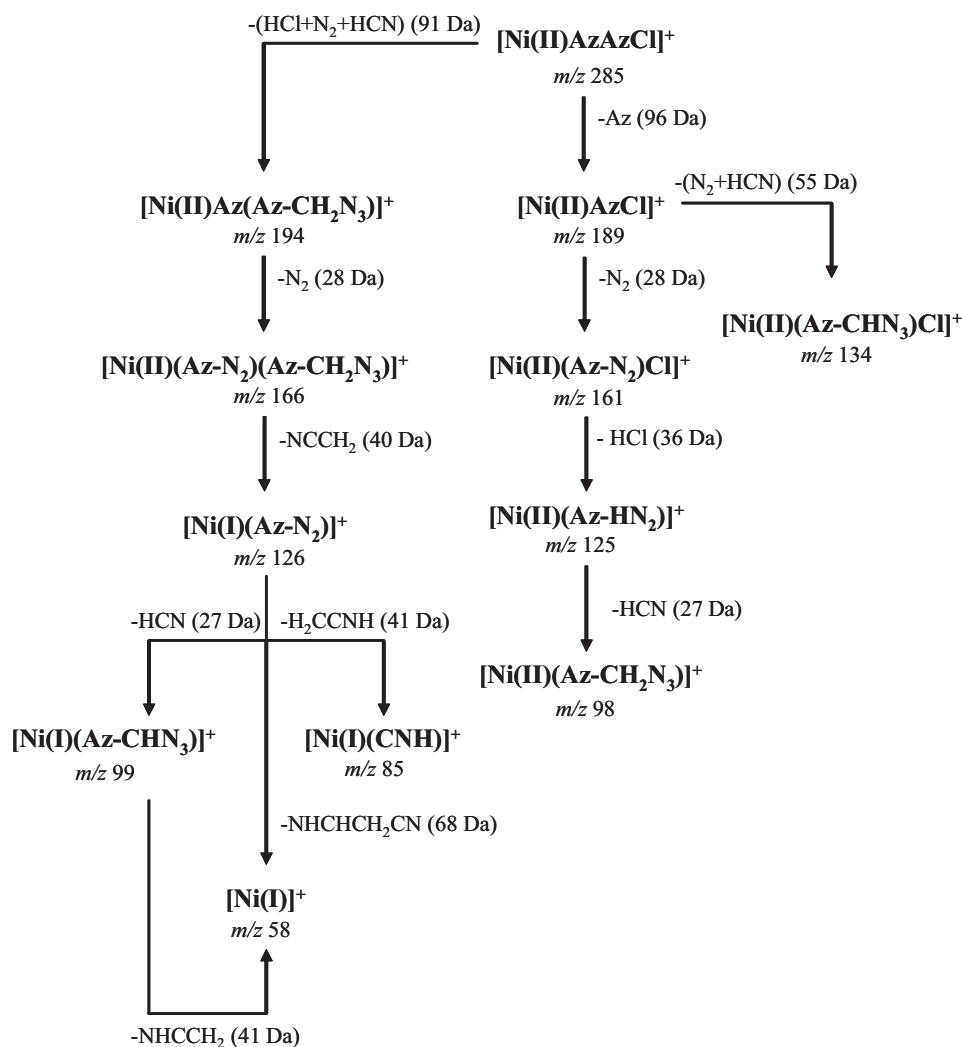
^aThe corresponding [M+2] ions have more than one contribution.^bThe corresponding [M+1] ion has more than one contribution.

trap involving the isolated ion were observed leading to water and methanol adduct ions (*M* + 18 and/or *M* + 32). There is evidence in the literature that these adducts are formed in the gas phase [50].

In Scheme 1, a sequential fragmentation of complexes formed from a NiCl₂ solution, starting with [Ni(II)AzAzCl]⁺ at *m/z* 285 and ending with terminal ions, is presented. These are at *m/z* 99, 85, 58 in one branch and *m/z* 98 in the other.

An important complex will be depicted as it does not appear in Scheme 1. This is a cluster species [Ni₂(II)AzAzCl₃]⁺ at *m/z* 413 (monoisotopic mass), whose MS-MS spectrum shows the most abundant daughter ion at *m/z* 285 [Ni(II)AzAzCl]⁺ by loss of 128 Da, which corresponds to NiCl₂. This observation is in agreement with work done, by Schröder et al. [51], on studies of binuclear cationic clusters of iron chloride. Structures including chloro-bridges between two metallic centers can be found in the coordination chemistry literature [52, 53] and may apply here. Another relevant factor that should be taken into account is the coordination site. Between ligands of the same type, bidentate ligands are more stable than monodentate ligands. Thus, it is expected that the 3-azidopropionitrile will behave as a bidentate ligand since in the azido and nitrile groups of this compound, electron pairs are available. Nevertheless, the possibility of 3-azidopropionitrile behaving as a monodentate ligand cannot be ruled out. In the literature [53, 54] two possible structures are reported for complexes of the type [Ni₂(II)L₂Cl₃]⁺, where L is ethylenediamine or bipyridyl,

(instead of 3-azidopropionitrile) in which the two nickel atoms have different coordination modes. To identify the coordination site by means of MS-MS analysis, it was decided to investigate in detail the fragmentation routes starting with a simpler ion than *m/z* 413. Scheme 1 starts with the complex at *m/z* 285, and two main fragmentation paths were found. In both, losses of N₂, HCN, HCl, occur although in different orders. No ambiguity remains on the loss of 28 Da from 3-azidopropionitrile, which is attributable to loss of N₂. In fact, previous studies on 3-azidopropionitrile [22] showed that the molecular ion loses N₂ but not H₂CN. In addition, there is agreement in the literature about the loss of N₂ as a first step of decomposition of organic azides [18–20]. The loss of HCl does not change the charge of the complex or the oxidation state of the metal as, apparently, a proton is donated by the ligand that becomes negatively charged. In one of the paths, as low masses (*m/z* 126, 99, 85) are approached, a redox reaction takes place and Ni(II) is reduced to Ni(I). This redox reaction seems to happen via a homolytic cleavage of a coordinate bond; consequently, a radical (e.g., NCCH₂) is released from the complex. This is, apparently, observed in the step from *m/z* 166 to *m/z* 126. A similar fragmentation pattern was observed when bromide was used as a counter ion. The only difference was that in some steps, Br[•] is released with simultaneous reduction of Ni, while loss of Cl[•] was not observed in Scheme 1. This different behavior might be explained on the grounds of relative values of bond dissociation enthalpy of HX (X = Cl, Br), which is higher for chlorine.

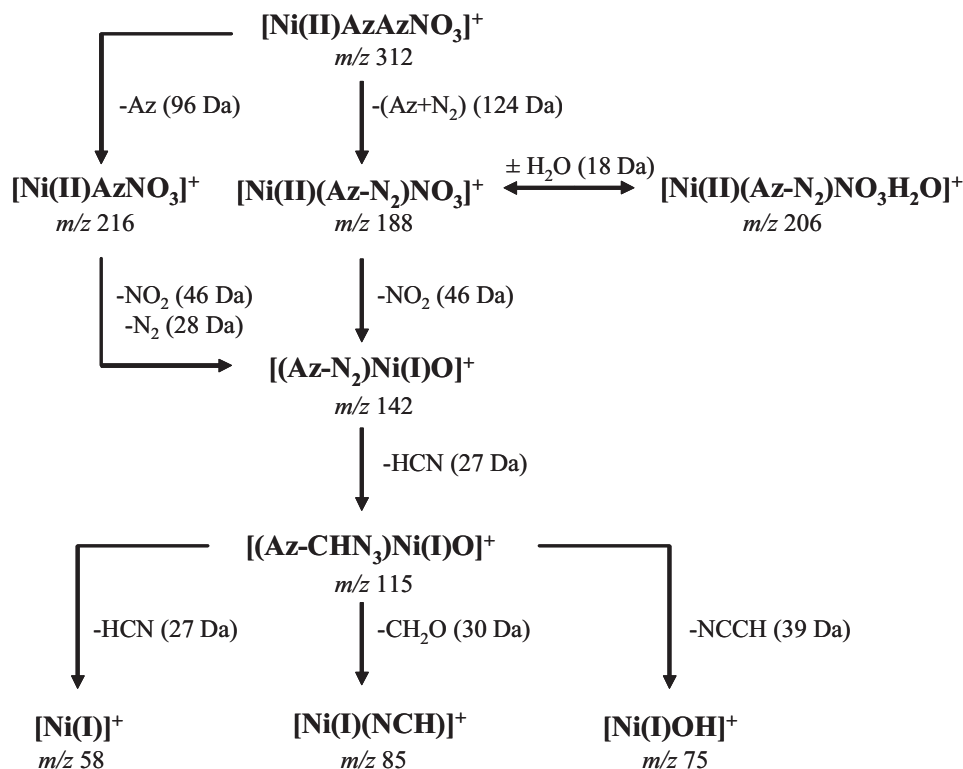


Scheme 1. Sequential fragmentation of some nickel complexes, from NiCl_2 solution, based on MS-MS experiments.

Continuing the analysis of Scheme 1, in the other main fragmentation path the nickel does not change its oxidation state since all the losses are neutrals. The terminal ions in this case are at m/z 125 and 98. The fragmentation scheme for the system with bromide as the counter ion is very similar to the previous one. The terminal ions are at m/z 126, 125, 99, 85, 58.

This study was extended to the counter ion NO_3 , first because its different nature from halide counter ions could help to understand the coordination process. Second, because Tsierkezos et al. [54] have claimed that its use would be a good test to the formation of Cl bridged complexes which should not occur when NO_3 is used. The complex $[\text{Ni}_2(\text{II})\text{AzAzX}_3]^+$ where $\text{X} = \text{Cl}$, Br , and NO_3 (Table 1) is more abundant for Cl and Br. The fact that the abundance of $[\text{Ni}_2(\text{II})\text{AzAz}(\text{NO}_3)_3]^+$ is approximately 3% is ambiguous since it can mean either that NO_3 bridged complexes exist, against predictions of Tsierkezos et al. [54], or that its low abundance points to a very unstable moiety. In any case, if there are bridged complexes in NO_3 , they are probably oxo-

bridged complexes. The complexes at m/z higher than m/z 142 (Scheme 2) have equivalent species in the previous fragmentation scheme. The terminal ions m/z 85 and 58 (Scheme 2) are coincidental with some seen before. On the other hand, some complexes with different compositions were detected at m/z 142, 115, 75, whose assignment was $[(\text{Az-N}_2)\text{Ni(I)O}]^+$, $[(\text{Az-CHN}_3)\text{Ni(I)O}]^+$, $[\text{Ni(I)OH}]^+$, respectively. Under these conditions, simple N—O bond cleavage in the nitrate ligand gives a ligated metal-oxide cation $[(\text{Az-N}_2)\text{Ni(I)O}]^+$ and the release of a radical NO_2 . As NO_3 is an anionic ligand, after homolytic cleavage of the N—O bond, leading to radical NO_2 , the remaining oxygen coordinated to nickel might carry one more electron than the usual number of valence electrons, which must be transferred to the metal yielding a reduced metal species. It is well known that metal monoxide cations of late transition metals, such as nickel, are very reactive and capable of activation of various substrates, with possible subsequent occurrence of oxidation reactions and rearrangements [48]. Thus, it is acceptable to admit



Scheme 2. Sequential fragmentation of some nickel complexes, from $\text{Ni}(\text{NO}_3)_2$ solution, based on MS-MS experiments.

that the ligand (Az-N_2) could be activated and attacked by the coordinate unit NiO^+ , yielding insertion products. In this work, the loss of CH_2O (Scheme 2) gives evidence for the occurrence of these processes.

In addition, similar species to $[\text{Ni(I)OH}]^+$ have been reported for iron [55] and thought to be formed by transfer of a hydrogen atom to $[\text{FeO}]^+$. A similar process for the formation of $[\text{Ni(I)OH}]^+$ is predicted. ESI-MS studies of Cu(II) -urea complex formation also reported the detection of the ion $[\text{Cu(I)OH}]^+$ [56].

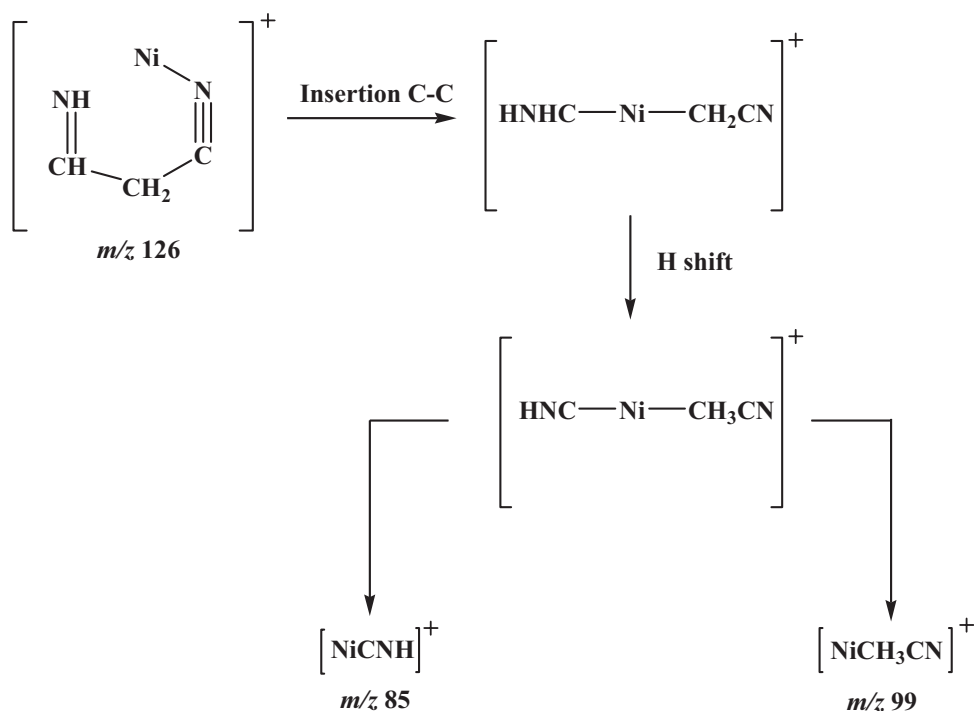
Complexes of the same type as seen for nickel were observed for cobalt. The most important complex ions have exactly the same assignments as for nickel but with one more Da per cobalt atom present. This cobalt investigation was made simpler by the absence of isotopic peaks from the metal. In Table 3, the correspondence of the species found for both metals can be verified. The results obtained from MS-MS analysis were also consistent with the nickel data. The main losses are also the same as already seen: N_2 , HCN, HCl, and radical NCCH_2 . The terminal ions have the same composition when compared with terminal ions in Scheme 1, with m/z values with one more Dal, i.e.: 127, 100, 86, 59, and 99.

At this stage, an attempt is made to explore the structure of these azido-complexes. For simplicity, this analysis will be based on complexes that originate from nickel chloride solutions; however, the reasoning will be applicable to species obtained with different counter ions and a different metal. Considering the

complex $[\text{Ni(II)AzAzCl}]^+$, the ion corresponds to the base peak of the spectrum, probably being a quite stable species. It loses one ligand azide (96 Da) yielding ion at m/z 189. Furthermore, considering the MS-MS of ion at m/z 189 (Scheme 1) two fragmentation routes can be followed. One of them implies the loss of $28 + 27$ Da, which only can be assigned in this compound as $\text{N}_2 + \text{HCN}$. Through the other route 28 Da are lost followed by 36 Da (HCl) and afterwards 27 Da (HCN). Comparing of both pathways, it can be concluded that the loss of 28 Da must be assigned to N_2 and not to H_2CN . This suggests that when the ligand 3-azidopropionitrile loses 28 Da, the loss was attributable to N_2 . It was mentioned above that this is an extremely common loss in organic azides. However, on looking at terminal complexes, doubts may arise about which atoms of the ligands were initially coordinated to the metal. CID experiments on their own may be limited by the inability to establish whether a fragment lost during CID was coordinated to the metal at the beginning or not [57].

The experimental data extracted from MS-MS studies are not conclusive on the coordination sites. To clarify this, some labeling and/or ion-molecule reaction studies would be necessary. In our case, it was decided to obtain some support from DFT calculations, the results of which will be presented in the next section.

Most of the literature on azides complexation with metals deals with metallic complexes with N_3^- anion present in inorganic azides. The scarce literature on organic azides does provide diverse evidence on ligand



Scheme 3. Mechanistic proposal for formation of ions of m/z 99 and 85 from ion m/z 126.

behavior in solution [32–34]. The first two studies report on a monodentate azide ligand being the terminal nitrogen of the azido group coordinated to the metal. The complex suffers loss of N_2 leading, by rearrangement and via an intermediate, to an imido complex. The third study describes a bidentate azide ligand involving coordination by two nitrogens, one of them the alkylated nitrogen of the N_3 group and the other a nitrogen from other functional group. Therefore, the available literature reports on different coordination types.

To attempt a deeper structural interpretation, it was decided to investigate one of the terminal ions $[\text{Ni}(\text{I})(\text{Az-N}_2)]^+$ (m/z 126) and its daughter ions of m/z 99 and 85. A mechanistic rearrangement is proposed (Scheme 3), which is based on a proposal by Eller et al. [58] and establishes a meaningful relationship among those ions. Complexation of the metal to the functional group XY (CN, NC) causes a C—C insertion of nickel followed by hydrogen shift (Scheme 3). From the intermediate formed, two ions can be derived, one of them keeps HNC strongly bound to the metal by elimination of the remaining part of the ligand (CH_3CN), the other keeps the part of the ligand coordinating the metal and loses HNC. This also applies to cobalt. Although it has been claimed that electrospray ionization is able to transfer solution species to the gas phase, one should bear in mind that this is a gas-phase mechanism.

To complete this study, another issue should be addressed, specifically to verify whether our data could be correlated with data obtained by FT-ICR. FT-ICR has also been applied to study the reactivity of azidoacetonitrile with anionic and cationic rhodium clusters [31].

Metal clusters show a gradual transition between gas-phase metal ion chemistry and surface-like behavior as the cluster size increases. Thus, for small clusters, a behavior with some degree of resemblance with our results was expected, in spite of the different metal and azidonitrile used.

For monoatomic Rh^+ , reacting with azidoacetonitrile, the following reactions were observed:



Similarly, for 3-azidopropionitrile complexes of nickel and cobalt, ligands were observed such as the intact azide and the remaining azide after loss of N_2 or HCN. Unlike monoatomic rhodium, no rhodium cluster showed the intact azidoacetonitrile. For clusters with $n > 3$, typical surface processes were detected, notably the formation of $\text{Rh}_n\text{C}_2\text{N}_2^+$ with N_2 and H_2 release from the molecule, carbene formation (Rh_nC_2^+ by release of 2N_2 and H_2) and Rh_nCN_2^+ or $\text{Rh}_n\text{C}_2\text{H}_2\text{N}_2^+$ formation.

Theoretical Study

Optimized B3LYP/6-31++G(d,p) structures for two conformers, A and B, of the $[\text{Ni}_2(\text{II})\text{AzAzCl}_3]^+$ complex are reported in Figure 1. For conformer A, the coordination number is four for both metal centers, which are connected by one chloro-bridge, and the azides play the

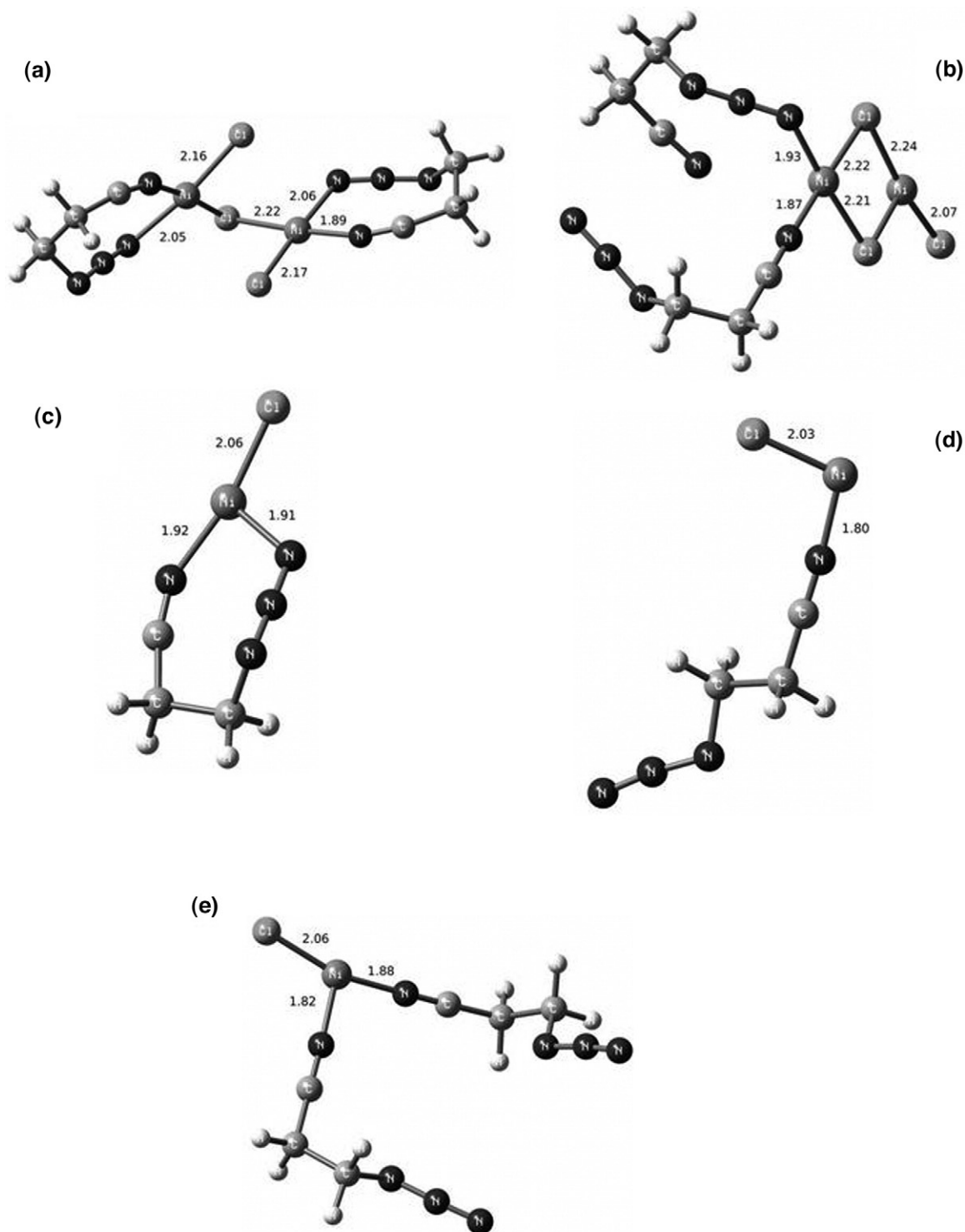


Figure 1. The structures of theoretical optimized complexes structures. (a) and (b) [NiAzAzCl₃]⁺ complex conformers. (c) and (d) [NiAzCl]⁺ complex conformers. (e) [NiAzAzCl]⁺ complex.

role of a bidentate ligand. In contrast to conformer A, the azides in conformer B play the role of a monodentate ligand. Interestingly, one of the azides is bound to Ni through the C—N group, whereas the other one is bound through the azide group. One metal center interacts with two Cl atoms and the coordination num-

ber is also 4 for one of the nickel atoms. On the other hand, the other metal center has a coordination number of 3, interacting only with chlorine ligands. For this conformer two chlorine bridges were present.

Some structural data for these complexes (bond lengths) are reported in Figure 1. From B3LYP/6-31 ++

G(d,p) calculations, the two conformers are nearly isoenergetic (conformer B is ~ 3 kJmol $^{-1}$ more stable than conformer A). Further information on the coordination chemistry of the complexes is provided by calculations on the smaller complexes [Ni(II)AzCl] $^{+}$ and [Ni(II)AzAzCl] $^{+}$.

The B3LYP/6-31 ++ G(d,p) optimized structures for two conformers, C and D, of the [Ni(II)AzCl] $^{+}$ complex are reported in Figure 1. Conformer C is a bidentate complex while conformer B is a monodentate complex, in which the coordination is established through the CN group. However, from B3LYP/6-311 ++ G(d,p)//B3LYP/6-31 ++ G(d,p) single-point energy calculations, the bidentate conformer C is 57.3 kJmol $^{-1}$ more stable than conformer D. Some structural data on these complexes are also reported in Figure 1. The Ni-NC bond length is 1.92 Å in conformer C. This distance is significantly smaller in conformer D (1.80 Å), reflecting a stronger interaction with the CN group in the monodentate structure. Although conformer C is energetically favored, a competition between the interaction of the metal center with the azide and nitrile groups leads to an increased Ni-NC distance in the bidentate complex.

The optimized structure of the [Ni(II)AzAzCl] $^{+}$ complex (e) is reported in Figure 1. In contrast to [Ni(II)AzCl] $^{+}$, for which a bidentate coordination was favored, the structure with two azides illustrates the formation of a structure with monodentate ligands. Although extensive searches on the potential energy surface have been carried out, no bidentate complex was found in this case. In addition, the two azides are bound to the metal center by the CN group. On the other hand, the structure (e) of Figure 1 seems to indicate that this complex is not energetically stabilized by the interaction between the azides. Apparently the structure of [Ni(II)AzAzCl] $^{+}$ reflects the feature that metal-ligand interactions are much stronger than ligand-ligand interactions. For example, the binding energy (BE) of the 3-azidopropionitrile dimer is 18 kJmol $^{-1}$ at the B3LYP/6-311 ++ G(d,p)//B3LYP/6-31 + G(d,p) level. However, the binding energy of NiCl to the azide (see Figure 1c) is 301 kJmol $^{-1}$. This value was not corrected for basis set superposition error (BSSE), but it is expected that BSSE is quite small for B3LYP/6-311 ++ G(d,p) calculations. The results of these binding energy calculations indicate that ligand-ligand interactions are much too weak to compete with metal-ligand interactions. In spite of much weaker ligand-ligand interactions than ligand-metal interactions, a refined sampling of the conformational space could be useful to assess local minima structures where ligand-ligand interactions are also optimized.

In agreement with experimental information on azide-metal complexes [32–34], the present theoretical calculations support the view that although bidentate complexes are energetically more stable, monodentate structures can also be observed in mono positively charged complexes involving 3-azidopropionitrile and

Ni. The specific structure of these complexes should reflect the fact that in comparison with metal-ligand interactions, ligand-ligand interactions are significantly weaker.

Conclusions

An electrospray study of solutions of Ni(II) and 3-azidopropionitrile, and Co(II) and 3-azidopropionitrile, yielded only single positively charged complexes, which were found to contain different ligands and various stoichiometries. The following ligands were detected in these complexes: the intact 3-azidopropionitrile, 3-iminopropionitrile, counter ions (Cl $^{-}$, Br $^{-}$, NO $_3^{-}$) of the salts used, and solvent molecules. The majority of complexes observed had one metal center and a general formula [M(II)Az $_n$ X] $^{+}$, where M = Ni or Co, X = Cl $^{-}$, Br $^{-}$, NO $_3^{-}$, and $n = 1$ –3. Cluster ions of the type [M $_2$ (II)Az $_n$ X $_3$] $^{+}$, ($n = 1$ –2), were also detected, being predicted to be halide-bridged binuclear complexes and oxo-bridged in the nitrate counter ion case. The most abundant complex ion had the general formula [M(II)Az $_2$ X] $^{+}$. A CID study followed by MS-MS analysis was performed to search for the coordination site(s). This analysis showed that losses of the intact 3-azidopropionitrile ligand are easily achieved for complexes with a large number of these ligands, either for the cluster or the complexes with only one metal center. Fragmentation of species of the general formula [M(II)-AzX] $^{+}$ and [M(II)(Az-N $_2$)X] $^{+}$ led to reduced metal species. Neutral losses, such as HCl and HBr, led to species where the oxidation state of the metal was retained. However, the elimination of radicals, Br or others, led to complexes, where metal reduction seems to take place due to homolytic cleavage of a metal–ligand bond. Elimination of the NO $_2$ radical, in the case of [Ni(II)(Az-N $_2$)NO $_3$] $^{+}$, yielded a ligated metal-oxide complex [(Az-N $_2$)NiO] $^{+}$, due to the specificity of the nitrate ligand. The reactivity of NiO $^{+}$ may be responsible for the activation and attack on (Az-N $_2$), leading to oxidation reactions and rearrangements, allowing losses such as CH $_2$ O. A mechanistic rearrangement, involving the insertion of the metal into C–C bond, followed by a H shift, is proposed for the terminal ion [M(I)(Az-N $_2$)] $^{+}$. The decomposition of the intermediate formed allows an explanation of the common terminal ions observed from the fragmentation sequences.

The MS-MS analysis was not totally conclusive on the coordination site. Nevertheless, the DFT calculations performed led to the conclusion that the 3-azidopropionitrile can act either as a monodentate or a bidentate ligand, with a variable coordination number for Ni. For the complex species under theoretical scrutiny, when the 3-azidopropionitrile ligand behaves as a monodentate ligand, the most favored functional group for coordination is the nitrile. In the case of the cluster [M $_2$ (II)Az $_2$ Cl $_3$] $^{+}$, the conformer B is not significantly more stable than A, however, there is an additional reason to support its occurrence. Under CID conditions,

NiCl₂ was the most important loss, which is more likely to occur from conformer B. These two conformers show some similarities with proposed structures in the literature [53, 54] for clusters of the same type. When the complexes are mononuclear, the metal coordination number is 2 or 3 whilst for binuclear complexes, the metal coordination number is 3 or 4. In this study, from the DFT calculations, it is clear that in complexes with the ligand 3-azidopropionitrile coordination never takes place via the alkylated nitrogen as was observed in previous studies. This can be explained since for the azide studied by Barz et al. [34], the coordination by the end-nitrogen is sterically hindered, while for 3-azidopropionitrile, the alkylated nitrogen is not accessible for bidentate coordination.

Concerning a possible comparison of our results with the results from a study by FT-ICR of the reactivity of azidoacetoneitrile with rhodium clusters, agreement is found between our results and the results obtained for small rhodium clusters.

Acknowledgments

The authors thank Professor Carlos Borges for kindly allocating experimental time on the mass spectrometer.

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